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(54) **Cemented carbide with a hardenable binder phase**

(57) The present invention relates to a sintered cemented carbide consisting of 50 to 90 wt-% submicron WC in a hardenable binder phase. The binder phase consists of, in addition to Fe, 10 - 60 wt-% Co, <10 wt-% Ni, 0.2 - 0.8 wt-% C and Cr and W and possibly Mo and/or V in amounts satisfying the relations

$$2x_C < x_W + x_{Cr} + x_{Mo} + x_V < 2.5x_C$$

where x denotes the mol fraction of elements in the binder phase and the following relation for the total Cr content

$$0.03 < \text{wt-\% Cr} / (100 - \text{wt-\% WC}) < 0.05.$$

In addition, the binder phase consists of martensite with a fine dispersion, a few percent, of coherent carbides, preferably of M_2C type, with a size of the order of 10 nm.

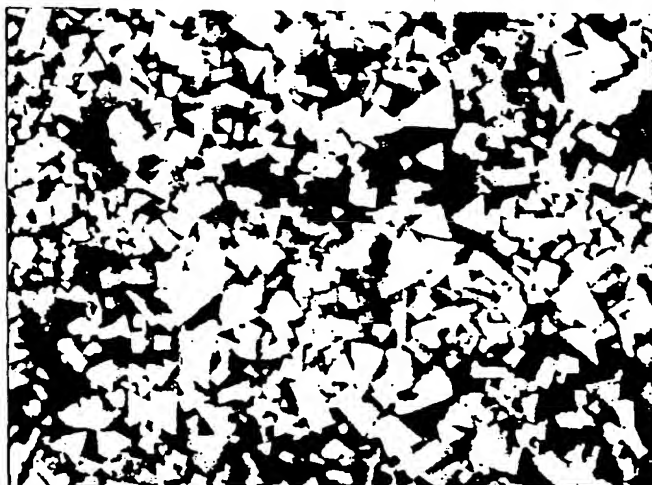


Fig. 1

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Description

[0001] The present invention relates to a material based on a hardenable binder phase, in submicron WC based cemented carbide.

[0002] It is desirable to develop cutting tool materials with a higher wear resistance compared to high speed steel and tougher than cemented carbide. One example of such a material is US 3,658,604, which discloses material containing 15 - 75 wt-% WC in a matrix of Co and Fe with a ratio Co to Fe of 0.65 to 2.0. Another example is US 4,145,213 which discloses 30 - 70 vol-% submicron hard constituents in a matrix of high-speed steel type.

[0003] The object of the present invention is to provide a hard material based on submicron WC in a hardenable binder phase.

[0004] It is a further object to provide a material with a balanced binder phase composition and hardening temperature. An efficient precipitation of secondary carbides requires a good balance between carbide formers and carbon dissolved in the hardened binder phase.

[0005] Fig. 1 shows a SEM micrograph of a material according to the invention, magnification X10000.

[0006] The material according to the present invention consists of 50 to 90 wt-% WC, preferably 60 to 75 wt-% WC, in a hardenable (martensitic) matrix. The WC has an average grain size of $<0.8 \mu\text{m}$, preferably $<0.4 \mu\text{m}$, with essentially all grains $<1 \mu\text{m}$. The hardenable binder phase contains Fe, Co and Ni with a Co content of 10 - 60 wt-% and a Ni content of $<10 \text{ wt-%}$, preferably $>0.5 \text{ wt-%}$. Further, the binder phase in addition to dissolved W must contain Cr and possibly Mo and/or V. The amount of dissolved W, Cr and Mo in the binder phase must balance the dissolved C at the hardening solution temperature such that

$$2x_C < x_W + x_{Cr} + x_{Mo} + x_V < 2.5x_C$$

where x denotes mol fraction elements in the binder phase. The carbon content of the binder phase must be 0.2 - 0.8 wt-% C, preferably 0.3 - 0.7 wt-% C. These requirements result in the following relation for the total Cr content of the material.

$$0.03 < \text{wt-\% Cr} / (100 - \text{wt-\% WC}) < 0.05.$$

[0007] The hardened binder phase consists of a martensitic matrix with a fine dispersion, a few percent, preferably more than 5 %, of coherent carbides, preferably of M_6C type, with a size of the order of 10 nm. The martensitic structure is body centred tetragonal (bct) and may contain up to 20 vol-% of face centred cubic metallic phase (fcc).

[0008] In a first preferred embodiment the material contains a binder phase with 10 - 15 wt-% Co. The C

content should be adjusted such that minor amounts of M_6C carbide is formed, 2 - 5 vol-%, less than $10 \mu\text{m}$ in size.

[0009] In a second preferred embodiment the material contains a binder phase with 45 - 55 wt-% Co. This embodiment avoids formation of M_6C carbide and other undesired phases such as graphite, M_{23}C_6 , M_7C_3 , M_3C_2 etc. The martensite formed in this embodiment is ordered which provides a further increase in hardness.

[0010] In a third preferred embodiment the material contains a binder phase with 5 - 10 wt-% Ni. This results in a precipitation of nanosize Ni-rich metallic fcc particles simultaneously with the carbide precipitation. Presence of the fcc particles, preferably 10 - 25 vol-%, significantly increases the toughness but somewhat decreases the hardness.

[0011] The material according to the present invention is made by powder metallurgical methods, milling, pressing and sintering. Suitable amounts of powders forming hard constituents and binder phase are wet milled, dried, pressed to bodies of desired shape and dimension and sintered.

[0012] The sintering is performed in the temperature range 1230 - 1350°C, preferably in vacuum. The first preferred embodiment requires an isothermal hold at about 1180°C for 2 h to form M_6C carbides with a desired size followed by sintering at a temperature where the binder phase is partially melted, 1230 - 1250°C, to avoid formation of too large M_6C particles. The second and third preferred embodiments can be sintered at temperatures where the binder phase is completely melted, 1280 - 1350°C.

[0013] After sintering the material is heat-treated. The material is solution treated in the range 1000 - 1150°C where the binder phase has a face centred cubic structure for about 15 min in protective atmosphere to dissolve carbide formers and some further W in the binder phase. The cooling from the solution temperature must be forced at a rapid temperature for from about 10 to 100 °C/sec in order to obtain a martensitic transformation, e.g. by oil quenching or similar. Finally, the material is heat treated one or more times in the range 500 - 650°C for about 1 h followed by forced cooling. The purpose of the final heat treatment is to obtain a dispersion of nanosized carbides of M_2C or MC type and to control the amount of retained face centered cubic phase.

[0014] Inserts according to the invention can be coated with thin wear resistant layers according to known technique, preferably PVD-technique.

Example 1

[0015] From a powder mixture comprising 31.4 wt-% Fe (BASF Iron CS), 4.8 wt-% Co (OMG Cobalt Extra Fine), 1.8 wt-% Cr_3C_2 (HC Starck), 61.6 wt-% WC (HC Starck DS 80, grain size $0.8 \mu\text{m}$) and 0.4 wt-% W turning inserts of type SNUN 120412 were pressed. The inserts were sintered with flowing H_2 up to 450°C for dewaxing,

further in vacuum up to 1180°C with a 2 h hold followed by sintering at 1240°C for 1 h.

[0016] The hardness after furnace cooling was 797 HV10. The inserts were held at 1100°C for 15 minutes and then quenched in oil resulting in a hardness of 1035 HV10. Double tempering, 1 h at 550°C, increased the hardness further to 1058 HV10.

Example 2

[0017] From a powder mixture comprising 15.4 wt-% Fe (BASF Iron CS), 15.4 wt-% Co (OMG Cobalt Extra Fine), 1.8 wt-% Cr₃C₂ (HC Starck), 67.3 wt-% WC (Dow Chemical SuperUltrafine, grain size 0.2 µm) and 0.1 wt-% carbon black turning inserts of type SEAN 1203AFN were pressed. The inserts were sintered with flowing H₂ up to 450°C for dewaxing, further in vacuum up to 1180°C with a 2 h hold followed by sintering at 1350°C for 1 h. See fig. 1.

[0018] The hardness after furnace cooling was 1088 HV10. The inserts were held at 1080°C for 15 minutes and then quenched in oil resulting in a hardness of 1216 HV10. Double tempering, 1 h at 550°C, increased the hardness further to 1289 HV10.

Example 3

[0019] The SEAN 1203AFN inserts of Example 2 were ground and coated with a 3 µm thick TiN layer according to known PVD-technique. Inserts of the same geometry with a high speed steel substrate (Alesa) and a submicron cemented carbide, WC + 13 wt-% Co, substrate (Seco Tools F40M) were coated in the same batch.

[0020] With the SEAN 1203AFN inserts single tooth milling tests were performed in an ordinary low carbon steel. The following data were used:

Speed = 125 m/min,
Feed = 0.05 mm/rev,
Cutting depth = 2.0 mm

[0021] The average lifetime for the high speed steel insert was 3 min, for the insert according to the invention, Example 2, 17 min and for the cemented carbide insert 40 min.

Example 4

[0022] From a powder mixture comprising 13.0 wt-% Fe (BASF Iron CS), 11.3 wt-% Co (OMG Cobalt Extra Fine), 1.9 wt-% Ni (INCO), 1.2 wt-% Cr₃C₂ (H.C. Starck), 72.0 wt-% WC (Dow Chemical Super-Ultrafine, grain size 0.2 µm) and 0.6 wt-% C turning inserts of type SNUN 120412 were pressed. The inserts were sintered with flowing H₂ up to 450°C for dewaxing, further in vacuum up to 1180°C with a 2 h hold followed by sintering at 1300°C for 0.5 h.

[0023] The hardness after furnace cooling was 1270 HV10. The inserts were held at 1100°C for 15 minutes and then quenched in oil resulting in a hardness of 1336 HV10. After double tempering, 1 h at 560°C, 600°C and 640°C, the hardness was 1351 HV10, 1294 HV10 and 1244 HV10 respectively.

Claims

1. Cemented carbide consisting of 50 to 90 wt-% sub-micron WC in a hardenable binder phase characterised in that said binder phase consists of, in addition to Fe, 10 - 60 wt-% Co, <10 wt-% Ni, 0.2 - 0.8 wt-% C and Cr and W and possibly Mo and/or V in amounts satisfying the relations

$$2x_C < x_W + x_{Cr} + x_{Mo} + x_V < 2.5x_C$$

where x denotes mol fraction elements in the binder phase and the following relation for the total Cr content

$$0.03 < \text{wt-\% Cr} / (100 - \text{wt-\% WC}) < 0.05.$$

2. Cemented carbide according to claim 1 characterised in that the binder phase contains martensite with a fine dispersion, a few percent, of coherent carbides, preferably of M₂C type, with a size of the order of 10 nm.
3. Cemented carbide according to claim 2 characterised in that the martensite is body centred tetragonal (bct) and contains up to 20 vol-% of face centred cubic metallic phase (fcc).
4. Cemented carbide according to any of the preceding claims characterised in that the a binder phase contains 10 - 15 wt-% Co and 2 - 5 vol-% M₆C carbide <10 µm in size.
5. Cemented carbide according to any of the preceding claims characterised in that the binder phase contains 45 - 55 wt-% Co, is free from M₆C, M₂₃C₆, M₇C₃, M₃C₂ with ordered martensite.
6. Cemented carbide according to any of the preceding claims characterised in that the binder phase contains 5 - 10 wt-% Ni with nanosize Ni-rich metallic fcc particles, preferably 10 - 25 vol-%.
7. Method of making a cemented carbide consisting of 50 to 90 wt-% submicron WC in a hardenable binder phase by powder metallurgical methods, milling, pressing and sintering of powders forming hard constituents and binder phase characterised

in that

- said binder phase consists of, in addition to Fe, 10 - 60 wt-% Co, <10 wt-% Ni, 0.2 - 0.8 wt-% C and Cr and W and possibly Mo and/or V in amounts satisfying the relations

$$2x_C < x_W + x_{Cr} + x_{Mo} + x_V < 2.5x_C$$

where x denotes mol fraction elements in the binder phase and the following relation for the total Cr content

$$0.03 < \text{wt-\% Cr} / (100 - \text{wt-\% WC}) < 0.05$$

- sintering is performed in the temperature range 1230 - 1350°C, preferably in vacuum, whereupon the cemented carbide is solution treated at 1000 - 1150°C for about 15 min in protective atmosphere; force cooled from the solution temperature e.g. by oil quenching and finally heat treated one or more times at 500 - 650°C for about 1 h followed by forced cooling.

8. Method according to claim 7 **characterised** in an isothermal hold at about 1180°C for 2 h followed by sintering at a temperature where the binder phase is partially melted, 1230 - 1250°C.

9. Method according to claim 7 **characterised** in sintering at 1280 - 1350°C.

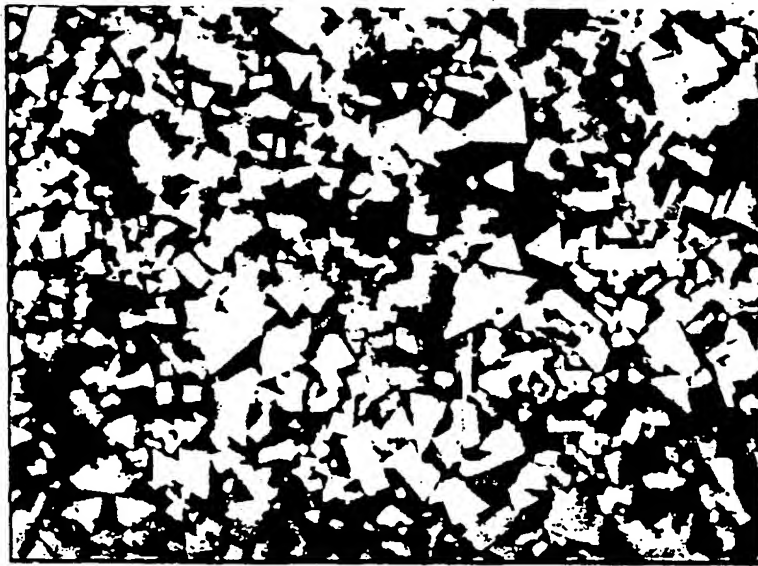


Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 1390

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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 April 2000	Examiner Gregg, N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 00 10 1390

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